HYDRAZINE AND HYDRAZINE SULFATE CAS Nos. 302-01-2 and 10034-93-2

First Listed in the *Third Annual Report on Carcinogens*

$$H_2N$$
— NH_2
 H_2N — NH_2

Hydrazine Sulfate

CARCINOGENICITY

Hydrazine and hydrazine sulfate are reasonably anticipated to be a human carcinogen based on sufficient evidence of in experimental animals (IARC V.4, 1974; IARC S.4, 1982; IARC S.7, 1987). When administered orally, hydrazine induced pulmonary adenomas and adenocarcinomas in mice. Intraperitoneal injection of hydrazine induced reticulum cell sarcomas of the mediastinum and myeloid leukemias in mice of both sexes (IARC V.4, 1974). When administered by inhalation, hydrazine induced alveolarogenic carcinomas, and lymphosarcomas of the spleen, in female mice (MacEwen et al., 1974). When administered orally, hydrazine sulfate induced pulmonary adenomas and adenocarcinomas, hepatomas, and hepatocarcinomas in mice of both sexes. When administered by stomach tube, hydrazine sulfate induced lung adenomas and adenocarcinomas in rats of both sexes and hepatic cell carcinomas and spindle cell sarcomas in male rats (IARC V.4, 1974).

Hydrazine

There is inadequate evidence for the carcinogenicity of hydrazine and hydrazine sulfate in humans(IARC S.4, 1982; IARC S.7, 1987). Two reports on cancer mortality among workers exposed to hydrazine have been published. One case of choroidal melanoma was observed in a man who had been exposed to hydrazine for 6 years. A study of 423 men engaged in the manufacture of hydrazine revealed three stomach, one prostate, and one neurogenic cancers. The evidence these studies provide was considered inadequate by an IARC Working Group.

PROPERTIES

Hydrazine is a white or colorless, oily, fuming liquid with an ammonia-like odor. It is miscible with water, methyl, ethyl, propyl, and isobutyl alcohols. Hydrazine is insouble in chloroform and ether. Hydrazine is a flammable liquid and may explode when exposed to heat, flame, or upon chemical reaction with alkali metals. When heated to decomposition, it emits fumes of highly toxic nitrogen compounds. Hydrazine is available as a propellant grade with a minimum of 97.5% purity. Solutions with varying hydrazine content are available for a variety of industrial uses.

Hydrazine sulfate is a colorless crystal. It is soluble in hot water and insoluble in alcohol. When heated to decomposition, it emits toxic fumes of sulfur oxides (SO_x) and nitrogen oxides (NO_x). Hydrazine sulfate is available in two grades of < 98% and 99% purity with heavy metal and chloride impurities.

USE

Hydrazine is used mainly as a chemical intermediate to produce agricultural chemicals, spandex fibers, and antioxidants. Hydrazine is also a rocket fuel, oxygen scavenger in water boiler and heating systems, polymerization catalyst, blowing agent, and scavenger for gases. Additionally, it is used for plating metals on glass and plastics and in fuel cells, solder fluxes, and photographic developers. Hydrazine is used as a reactant in fuel cells in the military, as a reducing agent in electrodless nickel plating, as a chain extender in urethane polymerizations, as a reducing agent in plutonium extraction from reactor waste, and as a water treatment (removal of halogens) chemical. Hydrazine is also used as a chemical intermediate for blowing agents, photography chemicals, pharmaceuticals, antituberculants, textile dyes, heat stabilizers, explosives, and hydrazine sulfate. (IARC V.4, 1974; Sax, 1987; HSDB, 1997).

Hydrazine sulfate is used in refining rare metals, as an antioxidant in soldering flux for light metals, in analytical tests for blood, and in the preparation of hydrazine hydrate. Hydrazine sulfate is also a biocide for fungi and molds, although there is no evidence that it is registered for use as a biocide in the United States. Investigators have studied hydrazine sulfate as an adjunct to antineoplastic drug treatment, but extensive use is not foreseeable (IARC V.4, 1974; Sax, 1987).

PRODUCTION

In 1986, the Chem Sources USA directory identified 28 suppliers and 1 producer of hydrazine and 31 suppliers and 1 producer of hydrazine sulfate (Chem Sources, 1986). No other current production data were available. In 1984, non-fuel production of 100% hydrazine was reported to be 20 million lb, while production capacity was 28 million lb. Production in 1982 and 1983 was reported to be 18 million lb; production in 1980 and 1981 was reported to be 19 million lb. Exports for 1980 through 1984 were reported to be 3 million lb. Demand was forecast to grow 3% annually from 1985 to 1989 (Chem. Prod., 1984b). The 1979 TSCA Inventory identified four companies producing 11 million lb of hydrazine in 1977 and 13 companies importing 660,500 lb. The CBI Aggregate was between 1 million and 100 million lb. The 1979 TSCA Inventory also identified seven companies producing 562,000 lb of hydrazine sulfate and three companies importing an unspecified amount (TSCA, 1979). Approximately 37.5 million lb of hydrazine were produced in 1974 (NIOSHa, 1978).

EXPOSURE

The primary routes of potential human exposure to hydrazine are ingestion, inhalation, and dermal contact. The National Occupational Hazard Survey conducted by NIOSH from 1972 to 1974 estimated that about 11,000 workers were possibly exposed to hydrazine in the workplace (NIOSH, 1976). In 1978, NIOSH estimated that 9,000 workers in the United States may have been potentially exposed to hydrazine and that over 90,000 may have been exposed to various hydrazine salts (NIOSHa, 1978). The environmental fate of hydrazine and its derivatives is largely unknown, but all the simple hydrazine derivatives are polar, nonvolatile, and soluble in water, resulting in possible drinking water contamination. Use of hydrazine in boiler water treatment may result in its occurrence in discharged waste, but it would react rapidly with oxygen. Possible ingestion of trace residues of hydrazine in processed foods is possible, although there is no known presence of hydrazine in consumer products. Hydrazine is a suspected contaminant of liquid formulations of isoniazid, a drug used to treat tuberculosis; FDA is investigating the magnitude of the problem to ensure that contamination of isoniazid is kept to

the lowest detectable limit. Hydrazine is also reported to occur in cigarette smoke at a concentration of 32 µg/cigarette (OSH, 1982). The Toxic Chemical Release Inventory (EPA) listed 45 industrial facilities that produced, processed, or otherwise used hydrazine in 1996 (TRI, 1996). In compliance with the Community Right-to-Know Program, the facilities reported releases of hydrazine to the environment which were estimated to total 10,716 lb. 10,443 lb total air release, 23 lb total water release, and 250 lb total land release. Only 2industrial facilities produced, processed, or otherwise used hydrazine sulfate in 1996 (TRI, 1996). They reported releases of hydrazine sulfate to the environment which were estimated to total 350,000 lb, all of which occurred via underground injection. Additional exposure information may be found in the ATSDR Toxicological Profile for Hydrazine (ATSDR, 1994f).

REGULATIONS

In 1980 CPSC preliminarily determined that hydrazine and hydrazine sulfate were not present in consumer products under its jurisdiction. Subsequently, public comment was solicited to verify the accuracy of this information; no comments were received. Pending receipt of new information, CPSC plans no action on this chemical. EPA regulates hydrazine under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Food, Drug, and Cosmetic Act (FD&CA), Resource Conservation and Recovery Act (RCRA), and Superfund Amendments and Reauthorization Act (SARA). Hydrazine is subject to report/recordkeeping requirements under CERCLA, RCRA, and SARA. A 1 lb statutory reportable quantity (RQ) has been established under CERCLA for hydrazine. Under FD&CA hydrazine is subject to regulations and data labeling requirements for its use as an inert ingredient of pesticides. If the threshold planning quantity of 1,000 lb established under SARA is reached, local response plans must be prepared. EPA regulates hydrazine sulfate under SARA, subjecting it to reporting requirements. FDA regulates hydrazine under FD&CA requiring that steam in contact with food contain no hydrazine. NIOSH considered a variety of serious health effects and recommended a reduction of the OSHA permissible exposure limit (PEL) from 1 ppm (1.3 mg/m³) as an 8-hr time-weighted average (TWA) to a 0.04 mg/m³ ceiling. The OSHA PEL is 0.1 ppm with a skin notation. OSHA regulates hydrazine under the Hazard Communication Standard and as a chemical hazard in laboratories. Regulations are summarized in Volume II, Table B-72.